COMPARATIVE ELECTROCHEMICAL STUDY IN COBALT AND COBALT-MOLYBDENUM COATINGS

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ABSTRACT

The paper presents results obtained in Co and Co-Mo coatings by electrodeposition on glassy carbon and copper electrodes. Many factors involved in the electrodeposition processes contribute to coating's high quality. The electrochemical aspects of the coatings were studied by cyclicvoltametry, cronoamperometry and cronopotentiometry measurements for understanding electrodeposition processes. The structure of the layers depends on the electrodeposition potential and time.

KEYWORDS: coatings, cobalt, cobalt- molybdenum alloy, electrodepossition, cyclic voltametry, structure

1. INTRODUCTION

One of the most important methods to increase the surface properties or to obtain new surface properties consist of thin specifiquel layers deposition by various methods, electrochemically, chemically, physically. The metal electrodeposition is a very important methods to improve surface resistance of materials because of their special properties, which make them suitable for applications such as coatings, decorating materials, metals recovery. There are many interpretation ways regarding the mechanism of electrocrystallization process.

The metal electrodeposition consists in the discharge of the metallic ion and it's deposition on the electrode. The stages of the deposition mechanism for each studied system are specific. The electrodeposition's kinetic on solid electrode states study the way in which metallic atoms must be incorporated during the solid surface phase formation, in order to be a part of an orderly and stable network. The chromium coatings were one of the most utilized systems in many fields because of their corrosion resistance properties, high temperature resistance and anti friction properties.

Because of the high toxicity of Cr (VI) is very important to find an opportunity to replace chromium coatings, obtained from the baths on the basis of its six-valence compounds. One possibility to solve this problem is refractory metals (Mo, W, V) utilization.

Due to relative availability of molybdenum and his properties, the greatest interest presents molybdenum alloys. So, was related that up to 20 of % (mass.) of Mo an alloy has a micro-hardness 500-1000 HV (after heat treatment), high corrosion resistance and good anti friction properties.

Despite of unsuccessful of direct electrodeposition of molybdenum, it can be codeposited easy with iron group metals (Ni, Co or Fe) forming alloys. The reduction mechanism of Mo is not so simply. Codepositation of molybdenum, require the formation of an intermediary compounds with iron group element, mechanism proposed by many authors [1-3]. The ions from iron group catalyze reduction reaction of molybdenum.

The reaction mechanism, where M represent iron group element (Ni, Co, Fe) and L is the ligand, in our case citrate ion, is as follows:

$$M_{(2)}L+e^- \rightarrow M_{(1)}L_{ads}$$
$$M_{(1)}L_{ads}+e^- \rightarrow M(s)+L$$
$$MoO_4^{2-}+M_{(2)}L+2H_2O+2e^- \rightarrow [M_{(2)}LMoO_2]_{ads}+4HO^-$$
$$[M_{(2)}LMoO_2]_{ads}+2H_2O+4e^- \rightarrow Mo(s)+M_{(2)}L+4HO^-$$

The stoekiometry for the species $M_{(2)}L\ MoO_2$ is not known.

2. EXPERIMENTAL DETAILS

The electroplated cobalt and Cobalt – Molybdenum alloy coatings were obtained.

Three experimental solutions were prepared, using an electrolyte with the following composition: $CoCl_2 \cdot 6H_2O$ 0.1 M; sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) 0.2 M. The solution containing only Co^{2+} ions was called A. Another's solutions called B, C and D contains Co^{2+} and Mo^{2+} ions. For the electrolytes B and C was added at the electrolyte A: Na_2MoO_4 0.05 M, pH=4, Na_2MoO_4 0.012 M, pH=5 respectively, and saccharin for electrolyte D. The electrolyte's preparation was utilized two-distilled and purified water with the Milique – Milipore system. The pH of solutions has been adjusted to the value of 4.0 and 5.0, with acid solution. The measurements were made with a pH-meter Metrohm 632 using standard buffers. The equipment used for electrochemical measurements was an Potentiostat 105 HQ Instruments coupled with a signals-generating set PAR 175 at a x-ray register Philips PM 8033, respectively a PAR 273, controlled by computer.

The conventional electrochemical cell used was of 100 mL volume, using three electrodes. The reference electrode (RE) was Ag/AgCl electrode Metrohm put into Luggin capillary, with a solution of saturated NaCl 1M. The auxiliary electrode (CE) was a spiral of Pt 99.99%. The working electrode (WE) was glassy carbon, with an area of 0.0314 cm^2, covered with a Teflon coating having the area of 0.07 cm^2. The preparation of the glassy WE before every experiment consisted in polishing it with solid alumina of 3.75 μm and 1.87 μm, washing it with distilled water by ultrasounds for two minutes. The next stage is putting the Teflon coating on the electrode. All experiments were performed in high purity argon atmosphere.

The electrolytes were magnetically stirred during the experiments, in order to keep the homogeneity of the suspensions.

3. RESULTS AND DISCUTIONS

a. Cyclicvoltammetry study

Cyclicvoltammetry studies were made for the solutions, which contain Co^{2+} ions only (electrolyte A), Co^{2+} and MoO_4^{2-} ions (electrolytes B and C), Co^{2+} and MoO_4^{2-} ions with saccharin additive (electrolyte D), under the same experimental conditions.

In the cyclicvoltammetry experiment (v=50mV/s) in case of electrolyte A, which contains Co^{2+} ions, a potential of -500 mV was used, with the cathode limit of -1132mV (Fig.1) and the anode limit of 200 mV. Under these circumstances, decreasing values of the peaks were registered. This means that, at this potential, the formation of deposition nuclei begins. A higher current intensity is necessary for the formation of the first nuclei. The process continues at smaller current intensities. In Fig.1 it can be observed a small peak in the anodic zone of the plot. Then is responsible for the oxidation reaction. Other tests were made between -1100 and 200 mV potential values. The formation of nuclei was registered at the same place and potential value, which proves it does not depend on the value at the initial potential.

From electrolyte B (Fig.2) a Co-Mo deposition was obtained. The range for the cathode limit was between –1060 mV and more negative with the concentration and pH from electro lyte B and C (Fig.3), –1096 mV, the potential depending on the values obtained for electrolyte A. In the solution D (Fig.4) witch have the saccharine additive, the value of potential of reduction is more negative (-1106mV). The reduction's process of the Co^{2+} and MoO_4^{2-} ions is more slowly because the saccharine is an inhibition for this process. The presence of MoO_4^{2-} ions requires more negative potentials for deposition. In this solution, MoO_4^{2-} ion discharges in a very small amount comparing with the Co^{2+} ions.

b. Cronoamperometry study

This cronoamperometry study is utilized in order to establish a better potential range for obtaining of Co and Co-Mo adherent deposits The current density curves were obtained for Co and Co-Mo deposits at different potential value which depend on the time of deposition.

Current density depends on the value of potentials. In the solution A at potentials more positive then –970, -1000mV, is observed a maximum of the current density.

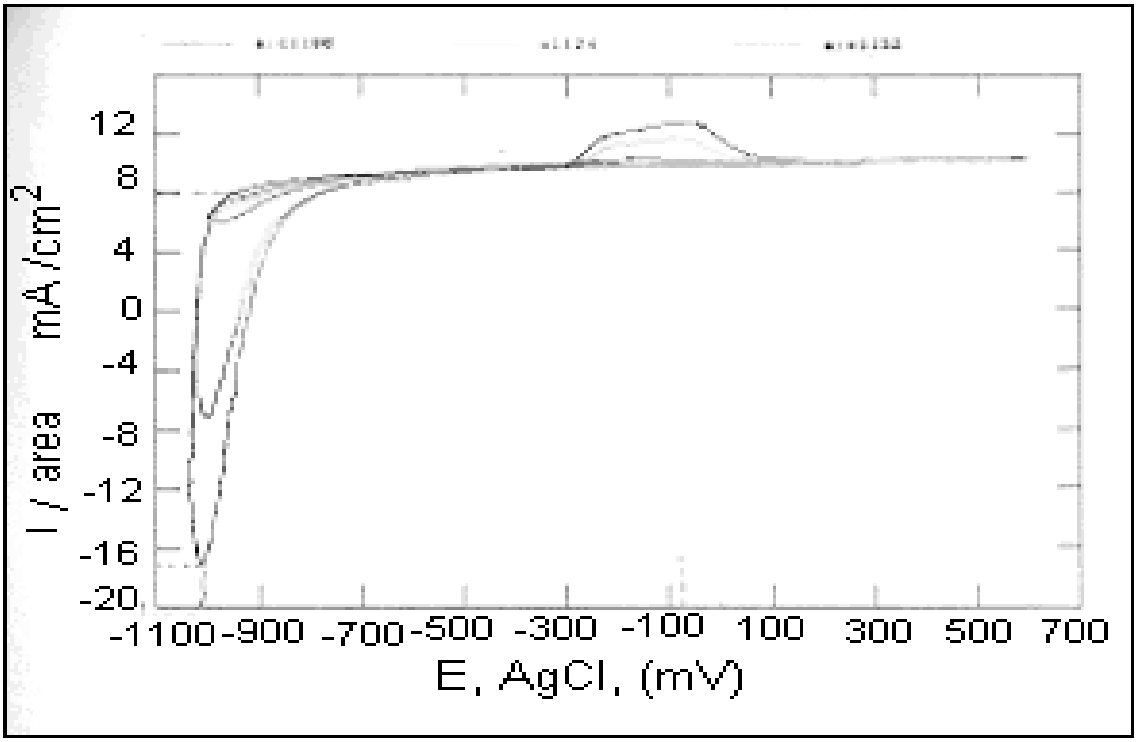

Fig. 1 The cobalt deposition voltamograme for electrolyte A

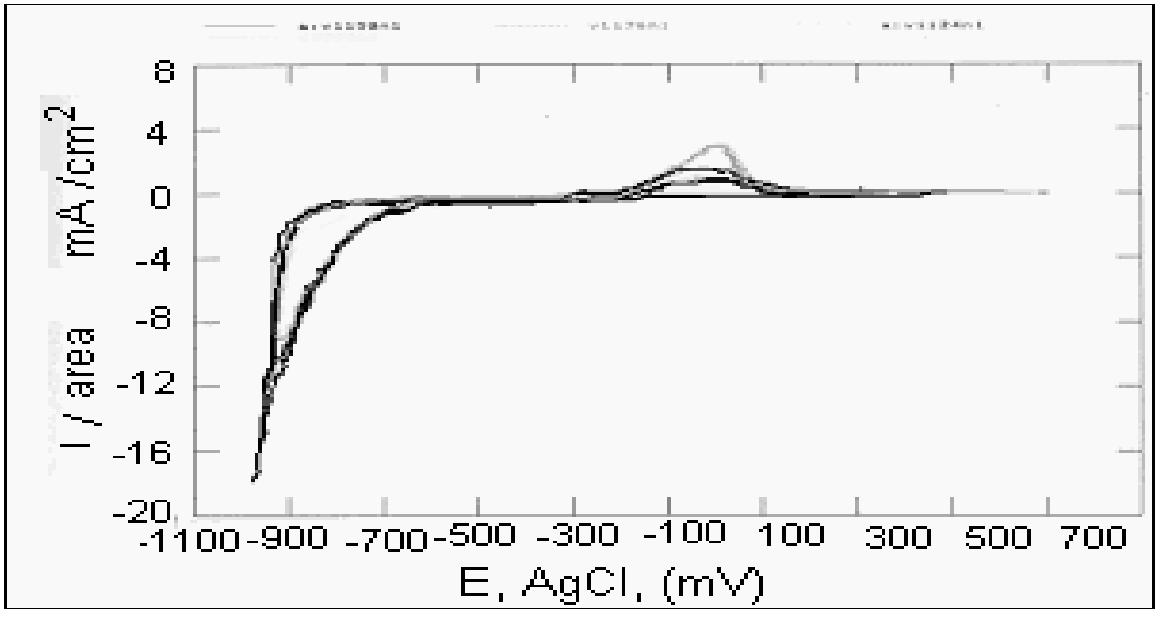

Fig. 2 The cobalt molybdenum deposition voltammograme from electrolyte B

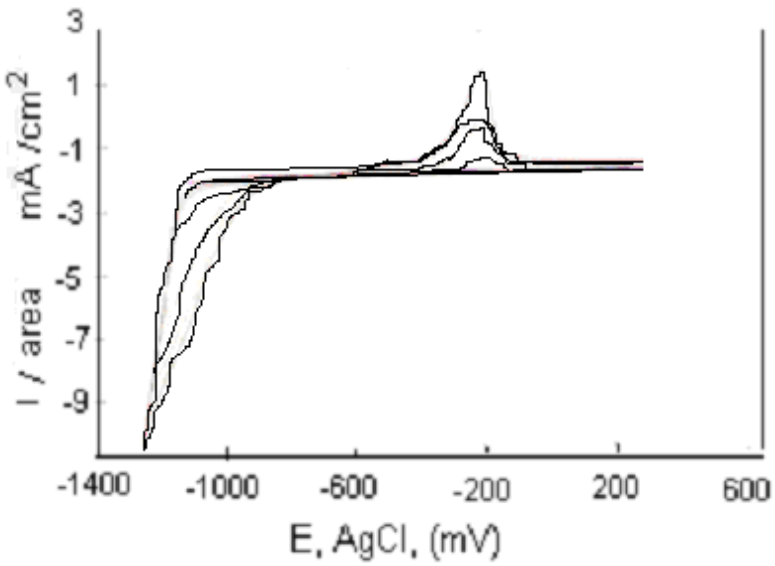

Fig. 3 The cobalt deposition voltammogram from electrolyte C

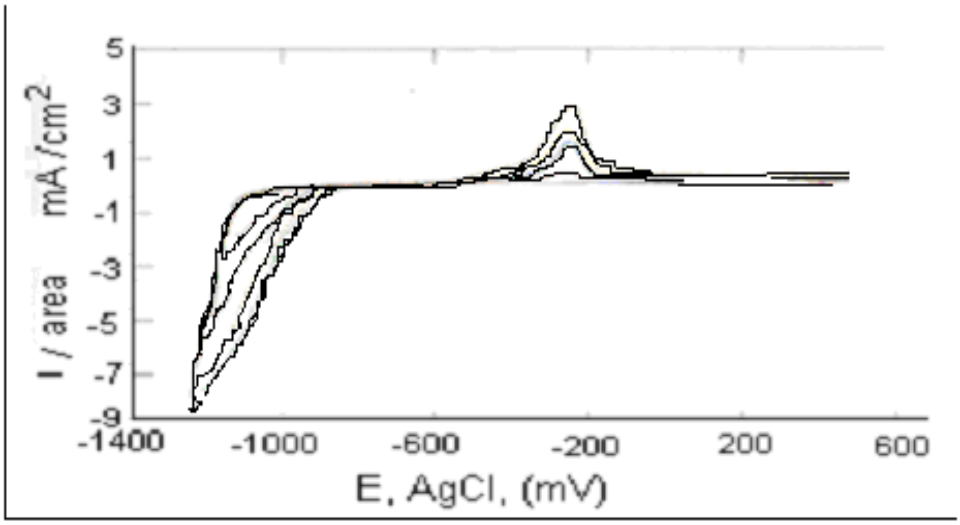

Fig. 4 The cobalt deposition voltammograme from electrolyte D

At values of potential more negative, a current density decrease was observed during coating's formation. The current density-time curves have the characteristic shape of a three-dimensional growth processes. The current intensity increases as a consequence of the nuclei's formation and of their growth.

The, Current density - time curve, fig. 5, obtained from the electrolyte B shows more positive reduction's potential, comparing with of the other electrolytes, because of the small concentration (0.005M) of MoO_4^{2-} ions, that means that for high concentration of MoO_4^{2-} ions it's necessarily more negative potential.

For the electrolyte D, with the saccharin (fig.6), the electrodeposition processes occur at more negative potentials with the attenuation of hydrogen discharge, due to saccharin's stabilizing effect.

An overview on results shows the following aspects:

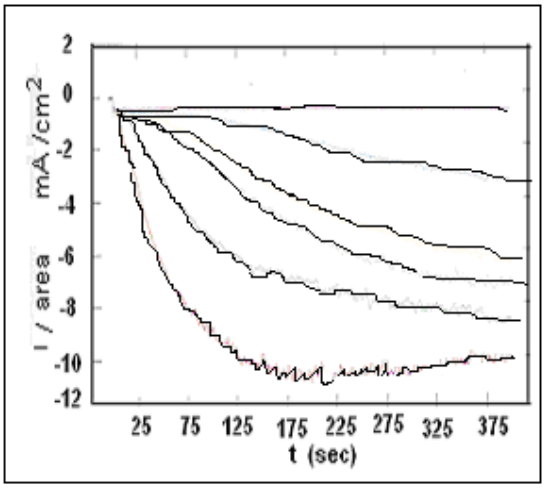

Fig.5. The cronoammperograme of Co-Mo electrodeposition from electrolyte B

- In electrolytes A, C and D the deposotion time diminish;
- for solution B the time is higher, because the concentrations of the two ions, MoO_4^{2-} and Co^{2+} , are small (0.005 M), the pH value is 4, so, the deposotion reaction occurs more difficult.

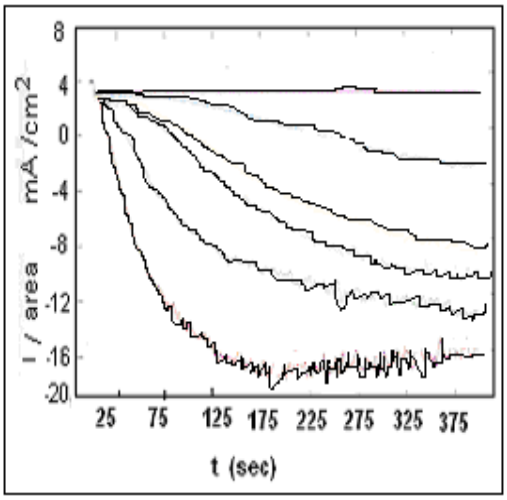

Fig.6 The cronoamperograme of Co-Mo electrodeposition from electrolyte D

c. Cronopotentiometry study

From the previous electrochemical studies was determined the optimum potential range of electrodeposition for Co and Co-Mo. Several coatings were obtained at different deposition time and at different current densities.

With rising of negative value of current density, the nucleation time is decreasing, therefore the nucleus forms easier. For example, in electrolyte D, the nucleation time $t_{nucletion}$ is 2.42 sec. at -10 μA and decrease to 0.403 sec at -100 μA.

The coatings obtained at more negative current densities are inhomogeneous and present a lot of defects.

From the potential- time curves obtained at -50 μA, can be observed that both potentials (nucleation and stabilization) are more negative for Co (fig 7) than for Co-Mo electrodeposition process, so, for Co $E_{nucleation}$ is -1221 mV, $E_{stabilization}$ is -923 mV and for CoMo alloy $E_{nucleation}$ is-1111 mV and $E_{stabilization}$ is -865 mV.

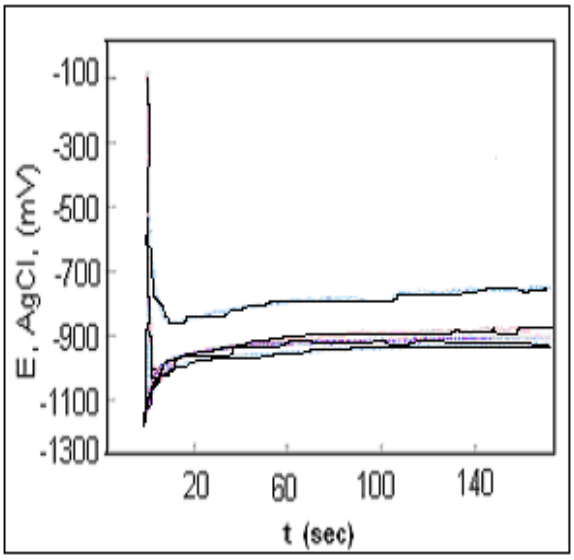

Fig.7 Potential-time dependency for cobalt electrodeposition from electrolyte A

The electrodeposition potential of CoMo alloy is more negative in the case of electrolyte D because saccharin which acts as an inhibitor hinders cathodic deposition (at -50 μA $E_{nucleation}$=-1153 mV and $E_{stabilization}$=-925 mV).

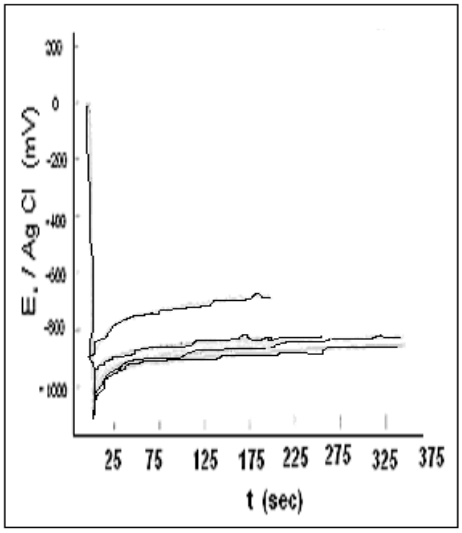

Fig.8. Potential-time diagram in Co-Mo deposition from electrolyte B

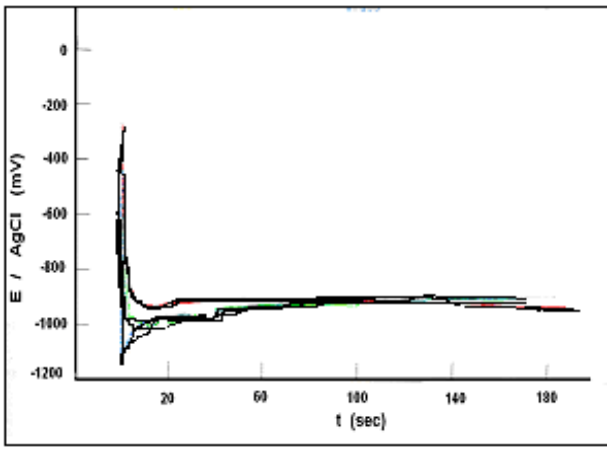

Fig.9. Potential-time diagram in Co-Mo deposition from electrolyte D

4. CONCLUSION

- Electrochemical method such as cyclic-voltammetry, cronoammperometry, and cronopotentiometry can be successfully used to characterize the Co-Mo electrodeposits obtained from sodium citrate electrolyte.
- The electrodeposition process in the Co-Mo system occurred at more positive potential values than pure cobalt deposits.
- The deposits in the Co-Mo system are formed by nucleation and three-dimensional rise mechanism.
- There were not any essential changes in the depositions obtained with and without stirring the electrolytes.
- Diffusion control of the process is progressive growing.
- The coatings obtained at more negative current intensities are inhomogeneous and present a lot of defects.
- The organic additives like saccharin have a positive influence on the coating's properties as chemical homogeneity, surface aspect, and brightness.
- Therefore, the organic additive utilization requires more electronegative potential values for Cobalt and Molybdenum electrochemical reduction reaction.

5. REFERENCES

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